Effect of Thickness on the Film Properties of Spray Deposited Copper Indium Sulfide Thin Films by Ultrasonic Impact Nozzle

Erkan Aydin*, Nurdan Demirci Sankir*,**‡, Hulya Unver*, Ezgi Uluer*

*Micro and Nanotechnology Graduate Program, TOBB University of Economics and Technology, Ankara, Turkey

**Department of Materials Science and Nanotechnology Engineering, TOBB University of Economics and Technology, Ankara, Turkey

‡ Corresponding Author; Nurdan Demirci Sankir, Sogutozu Caddesi, No:43, 06560 Ankara, Turkey, +90 312 292 4392,nsankir@etu.edu.tr, eaydin@etu.edu.tr, hyalcin@etu.edu.tr, euluer@etu.edu.tr

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Abstract- In this study, copper-indium-sulfide ($CuInS_2$) thin films were deposited on soda lime glass substrates using ultrasonic spray pyrolysis (USP) technique from the aqueous solution of Copper(II)chloride-dehydrate ($CuCl_2$), indium(III)chloride ($InCl_3$) and thiourea (NH_2CSNH_2). To investigate the effect of film thickness, different solution amounts were sprayed. As expected, the thickness of the films increased with increasing the amount of solution used. It has been obtained that thickness of the $CuInS_2$ absorber layer is critical for structural, morphological and optical properties. Crystal structure of the spray-deposited films was confirmed using X-ray Diffraction (XRD) analysis. The crystallite size of the films was ranging between 12.37 and 26.72 nm. X-ray photoelectron spectroscopy (XPS) study revealed that Cu concentration in the films increased by increasing the solution amount. Surface morphology of the films was investigated via scanning electron microscope (SEM). All sprayed films were defect free. Moreover, Cu rich-island formation was observed on the surface of $CuInS_2$ films sprayed using solutions more than 20 ml. Optical band gap energy of the films decreased from 2.85 to 1.40 eV with increasing the solution amount. As a result, thin films deposited using 30 ml solution was superior to others in terms of structural and optical properties. Moreover, it is very important to mention here that the ultrasonic impact nozzle used in this study enabled using very little amount of solution (0.015 ml/mm^2), which is approximately 10 times lower than solution reported previously. This promising result can be the key for large-area manufacturing of $CuInS_2$ based solar cells.

Keywords- Thin film solar cells; spray pyrolysis; chalcopyrite semiconductors; copper indium sulfide; low cost solar cell

1. Introduction

Thin films have been used extensively in photovoltaic devices due to their unique properties such as less material need and better device performances [1]. $CuInS_2$ is one of the I-III-VI_2 chalcopyrite-type mixed crystal semiconductor. $CuInS_2$ as an absorber layer is very promising for thin film photovoltaic applications because of its direct band gap energy of 1.53 eV and high absorption coefficient [2]. Siemer et al. reported sputtered $CuInS_2$ solar cells with % 11.4 record efficiency in 2001 [3]. It is very critical to increase the efficiency/production cost ratio for thin film solar cell applications [4]. With this motivation numerous methods have been applied to deposit $CuInS_2$ thin films such as reactive magnetron sputtering [5], a combination of evaporation and sulfurization processes [6], chemical bath deposition [7], flash evaporation [8] and spray pyrolysis [9]. Among these methods spray pyrolysis (SP) technique has been investigated extensively because it is a very simple, and therefore, cost-effective method [10, 11]. It also allows deposition of thin films on very large areas.

SP technique was first used in 1966 by Hill and Chamberlin to produce thin films of certain inorganic sulfides and selenides [12]. Since then SP has been using to deposit a wide variety of thin films. The application areas of

these thin films include solar cells, sensors, and solid oxide fuel cells [13]. Physical and chemical properties of the spray deposited $CuInS_2$ films depend strongly on the process parameters, such as substrate surface temperature and stoichiometry of the precursor solution [13]. Effects of substrate temperature [10] and stoichiometry [11] have been extensively studied. According to our best knowledge this is the first report on the effect of thickness on the film properties of $CuInS_2$ deposited via SP system equipped with ultrasonic impact nozzle.

2. Experimental Methods

The $CuInS_2$ thin films deposited using $CuCl_2$ (Sigma-Aldrich), $InCl_3$ (Sigma-Aldrich), NH_2CSNH_2 (Acros Organics) as a copper, indium and sulfur source, respectively. Aqueous precursor solution was sprayed on preheated soda lime glass substrate (26x76x1 mm^3). Prior to deposition glass substrates were cleaned with Alconox® solution and acetone. Substrate temperature was kept constant at 350 °C during all experiments. After deposition, samples were allowed to cool at room temperature. The molar ratio of the Cu/In/S in solution and infuse rate were also kept constant for all samples at 1/1/3 and 1.5 ml/min, respectively. Nitrogen was used as the carrier gas at 4.6 MPa pressure. Process time was ranging between 25 and 90 min depending on the solution amount. The crystal structure of the films was confirmed using Panalytical, X'pert Pro MPD XRD. The surface morphology of the films was investigated by FEI, Quanta 200 FEG SEM. Chemical structure of the $CuInS_2$ samples has been determined via XPS (Thermo, K-Alpha - Monochromated high performance XPS spectrometer). The optical transmittance was recorded in wavelength range of 200-3300 nm using a Varian Cary 5000 UV-VIS-NIR spectrophotometer. Electrical measurements were conducted via Keithley 2400 I-V source measure system.

In this study Sono-Tek FlexiCoat USP System was used to deposit $CuInS_2$ thin films. Spraying system consists of an impact nozzle, syringe pump, substrate heater, and temperature controller. Schematic structure of USP system used here is illustrated in Figure 1.

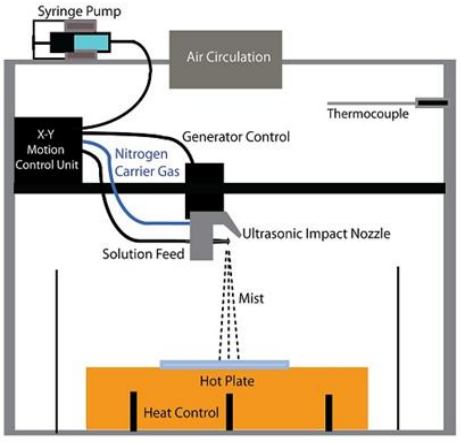

Fig. 1. Schematic illustration of USP system equipped with SonoTek ultrasonic impact nozzle

Spray pyrolysis is basically a chemical process. It is a well-known fact that properties and homogeneity of the films strongly depend on the nozzle type. A new generation impact nozzle has been used in this study. With this system, precursor solution is ultrasonically excited using piezoelectric crystals to generate very fine droplets. Droplet size, which is in micron size range, can be controlled by the oscillation frequency of the crystal. The droplets are transported by a carrier gas onto a heated substrate, where the precursor thermally decompose and form thin film. Nozzle head can scan substrate throughout X and Y dimensions with the help of PathMaster® software. Substrate temperature can be controlled with an accuracy of ±5 °C by using PID control system.

3. Results and Discussions

3.1. Structural Properties

SEM micrographs of the $CuInS_2$ films prepared with different solution amounts are presented in Figure 2. As can be seen in this figure all samples were pin-hole and crack free. Cross sectional SEM studies showed that, thickness of the films increased by increasing the solution amount as expected. However, surface of 30 ml and 40 ml sprayed films contains some agglomerated round shapes. Density of agglomerated areas and surface roughness of the films increased with increasing the solution amount. Energy Dispersive X-Ray Analysis (EDAX) has been used to determine the chemical structure of both flat and agglomerated regions on the $CuInS_2$ films. It has been observed that the chemical composition of the island like structure was copper (Cu) rich. It is possible to conclude that when the solution amount, and therefore the production time increased, Cu diffused through the surface and formed Cu_xS phases. Sherer et al. have been reported the formation of similar island like Cu_xS phases on the surface of co-evaporated $CuInS_2$ films [14].

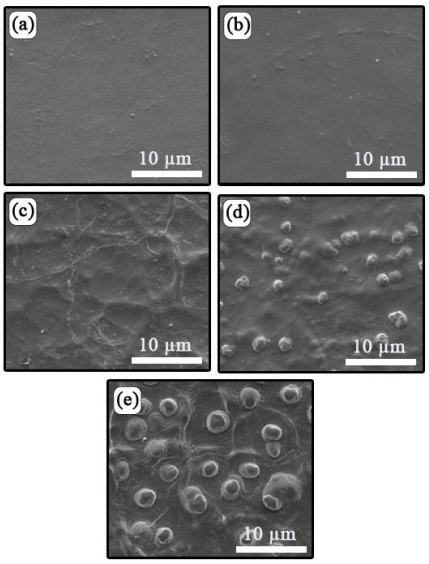

Fig. 2. SEM micrographs of $CuInS_2$ thin films deposited with a) 5 ml, b) 10ml, c) 20 ml, d) 30 ml, e) 40 ml precursor solution.

XRD patterns of the films deposited with different solution amounts at 350 °C plate temperature are shown in Figure 3. We have obtained the typical X-ray diffraction peaks of chalcopyrite structure regardless of the solution amount (JCPDS no. 27-159). All sprayed films showed two major peaks around 27.9° (2θ) and 46.3° (2θ). Besides, two minor peaks around 32.3° (2θ) and 54.6°(2θ) were observed for 20 ml, 30 ml and 40 ml solution sprayed films. Crystallinity of the films increased with solution amount. The reason of this improvement in crystallinity could be both the increase in deposition time and the thickness of the films with increasing the solution amount.

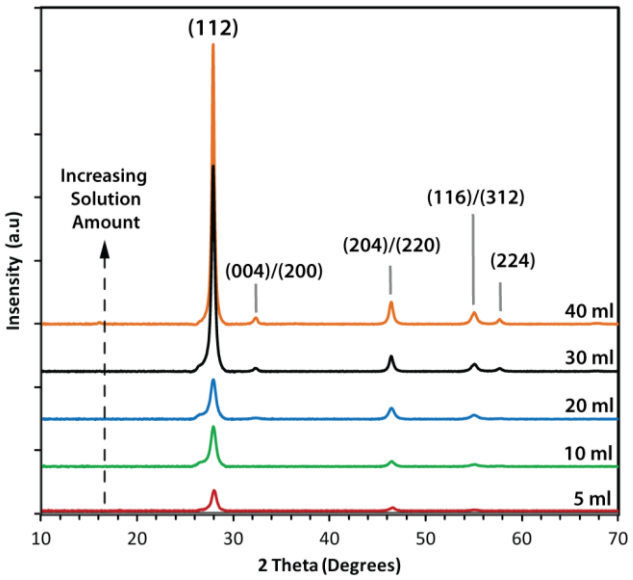

Fig. 3. XRD of ultrasonically sprayed $CuInS_2$ films prepared at different solution amounts.

The crystallite size of the films were calculated using the most intense diffraction peak observed around 2θ = 27.9° using well known Debye-Scherrer formula;

$$d = \frac{0.89\lambda}{\beta Cos\theta} \quad (1)$$

where d is the crystallite size; λ is the X-ray wavelength used; β is the angular line width of half maximum intensity; and θ is the Bragg's angle. As a general trend, mean crystallite size and peak intensity of the films increased with increasing the solution amount (Table 1). The calculated values of crystallite size were ranging between 12.37 nm and 26.72 nm. As can be seen in Table 1 crystallite size of the $CuInS_2$ thin films did not changed much for the solution amount ranging between 5 and 20 ml. However, crystallite size of the films increased when the spray solution amount exceed 30 ml. Previously T. Sebastian et al. [15] and M. A. M. Khan et al. [16] reported similar crystallite sizes for the spray pyrolysed $CuInS_2$ thin films.

The chemical compositions of the films evaluated by EDAX were presented in Table 2. The EDAX microanalysis was carried out at accelerating voltage of 15 kV and spot size 3μm. Measurements were done over large areas (300 μm x 300 μm).

Table 1. Some structural properties of $CuInS_2$ films.

Solution Amount (ml)	Film Thickness (μm)	Mean Crystallite Size (nm)	(112) Peak Intensities (a.u.)
5	0.28	13.63	6373
10	0.68	12.70	12600
20	1.27	12.37	12378
30	1.95	20.77	64901
40	2.25	26.72	88361

EDAX results represent the average value of two different regions. According to EDAX results all sprayed films are sulfur rich and contain Cl contamination up to 4.6 %. Presence of chlorine is due to the use of chloride based precursors for deposition. 10 ml solution sprayed films were In rich. This may be the reason of high resistivity of these films. High resistivity of the In rich films have been previously reported by other authors [17]. Except the films deposited using 10 ml solution, all samples were Cu rich so they showed high electrical conductivity under dark conditions. Although, there were some deviations, we obtained very close Cu, In, S ratios to the targeted 1:1:2 value.

Table 2. Elemental composition from EDAX of as-deposited $CuInS_2$ films

Solution Amount (ml)	Cu (At %)	In (At %)	S (At %)	Cu/In Ratio	S/In Ratio
5	13.3	11.7	30.9	1.13	2.64
10	19.9	22.3	46.5	0.89	2.09
20	23.1	22.8	50.3	1.01	2.21
30	23.1	22.1	50.2	1.05	2.27
40	24.0	21.7	50.3	1.11	2.32

XPS spectra of the films were recorded employing argon ion sputter etching for 30 seconds. Figure 4 shows the XPS spectra of Cu2p3/2, In3d5/2 and S2p core levels of sprayed $CuInS_2$ films. According to these spectra of sprayed solution with Cu/In/S=1/1/3 stoichiometry on 350 °C heated substrate, binding energies Cu2p3/2, Cu2p1/2, In3d5/2, In3d3/2 and S2p were 932.5, 952.6, 444.9, 452.5, 161.9 eV, respectively. The recorded binding energies were in good agreement with that of copper, indium and sulfur in spray deposited $CuInS_2$ films in literature [10].

3.2. Optical and Electrical Properties

Figure 5 shows the transmittance versus wavelength plots of the $CuInS_2$ films deposited using various amounts of precursor solution. As expected transmittance of spray deposited films decreased with increasing the spray solution volume. 5 ml and 10 ml solution sprayed films showed absorption edge at shorter wavelengths than others. Transmittance of sprayed films decreased with further increase in solution amount, due to both change in the thickness and change the structure of the film. Absorption coefficient and band gap values for sprayed $CuInS_2$ films were determined from the optical transmission data. The absorption coefficient of 10ml, 20ml, and 30ml solution

sprayed films is close to ~10^5 cm^{-1} starting from the wavelengths 980-1000 nm. This feature confirms that sprayed films are suitable candidates for absorber layers of photovoltaic applications [11].

Band gap values of the sprayed $CuInS_2$ films were calculated using UV-vis-NIR data. For an allowed direct band gap transition, the absorption coefficient can be related to the photon energy hν by;

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2} \quad (2)$$

where A is a constant, and E_g is the energy gap. It has been observed that band gaps of $CuInS_2$ films decrease with increasing solution amount as a general trend.

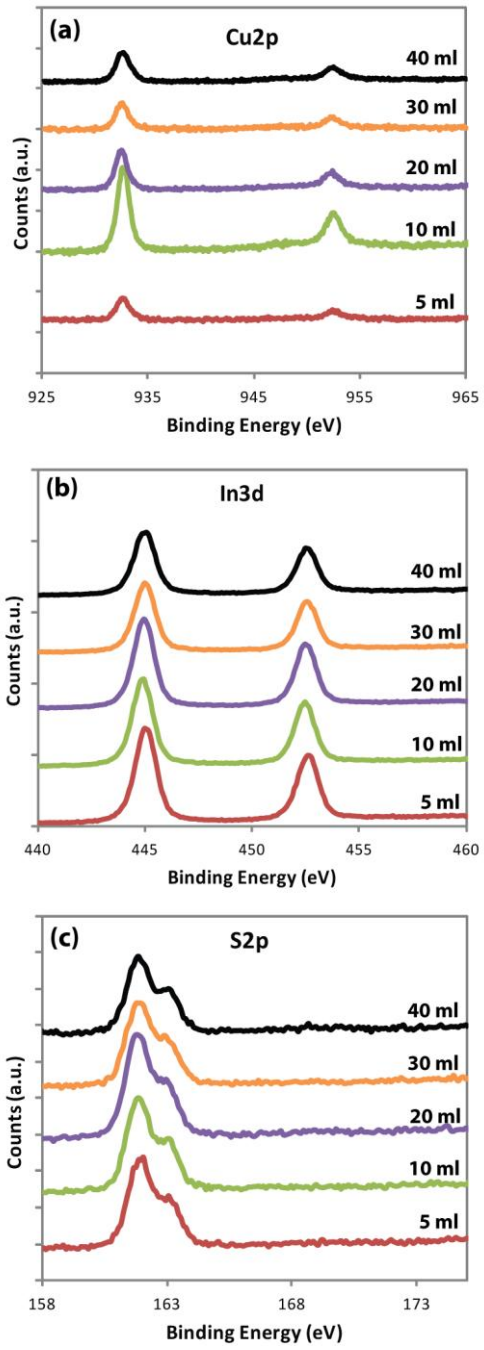

Fig. 4. High-resolution XPS spectra of (a) Cu2p, (b) In3d, (c) S2p regions of $CuInS_2$ thin films

The band gap of the films deposited with 20 ml solution was 1.45 eV which is very close to Eg of bulk $CuInS_2$ which is 1.53 eV (Table 3).

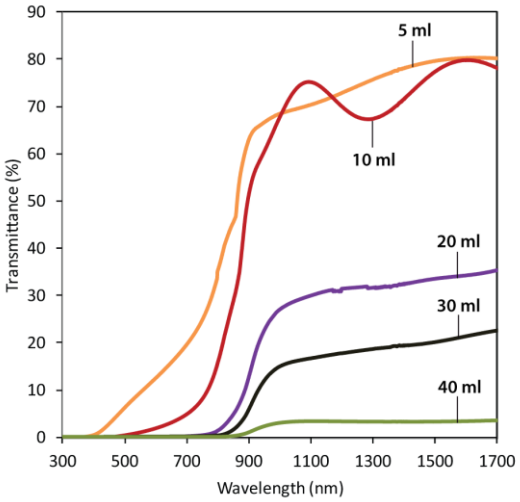

Fig. 5. Transmittance vs wavelength plots of $CuInS_2$ thin films deposited with a) 5 ml, b) 10ml, c) 20 ml, d) 30 ml, e) 40 ml precursor solution.

Room temperature bulk resistivity measurements of the films were done via 2 point-probe technique. Silver strips were sputtered on the films with 2.5 mm distance between them. Bulk resistivity values were calculated using the following well-known equation;

$$\rho = \frac{R.A}{l} \quad (3)$$

where ρ is the resistivity, R is the resistance, and A is the cross-sectional area of the film. Table 3 summarizes the sheet and bulk resistivities of the $CuInS_2$ films prepared in this study. Between 10 ml and 30 ml solution sprayed films the bulk resistivity decreased with increasing the solution amount. This can be explained by high crystallinity of thicker films. However, 40 ml solution sprayed samples showed higher bulk resistivity most probably due to the different trap mechanisms across the thick film profile.

Table 3. Some optical and electrical properties of $CuInS_2$ films

Solution Amount (ml)	Band Gap (eV)	Sheet Resistivity (Ω/□)	Bulk Resistivity (Ωm)	PS $(I_L-I_D)/I_D$
5	2.85	5.46 x10^5	2.42x10^{-1}	0.4
10	2.70	1.44 x10^6	8.85x10^{-1}	1.0
20	1.45	6.15 x10^5	5.58x10^{-1}	0.9
30	1.38	4.37 x10^5	3.27x10^{-1}	1.5
40	1.40	3.80 x10^5	10.1x10^{-1}	1.2

Sheet resistivity measurements of the films were conducted by Lucas Lab S-302 4-point probe analyzer equipped with Keithley 2400 I-V source meter. Sheet resistivity of the $CuInS_2$ films deposited using 5 ml solution was 5.46 x10^5 Ω/□. This value decreased to 3.80 x10^5 Ω/□ when the sprayed solution amount increased to 40 ml. The

reason of this decrease in resistivity was probably the Cu_xS phases formed on the surface (Figure 6).

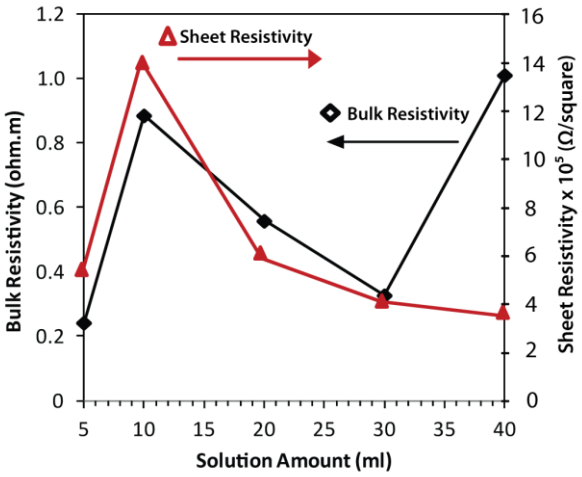

Fig. 6. Variation of resistivity of the films with different amount of solutions

In order to determine the photosensitivity (PS), samples were illuminated using Lot-Oriel solar simulator with 150W Xenon short arc lamb mounted. PS values calculated using the following formula:

$$PS=(I_L - I_D)/I_D \quad (4)$$

where I_L represents the current under illumination and I_D represents the dark current. Figure 7 shows the variation in PS with solution amount. All sprayed films showed very low PS values ranging between 0.4 and 1.5. The maximum PS was observed for 30 ml solution sprayed films. It can be concluded that PS of $CuInS_2$ is not directly related to the solution amount. Aforementioned, Cu amount in the films increased with increasing sprayed solution volume. Cu rich films showed better crystallinity as shown XRD spectra (Figure 3). Better crystallinity and low resistivity of the Cu rich films could be the reason of low photosensitivity.

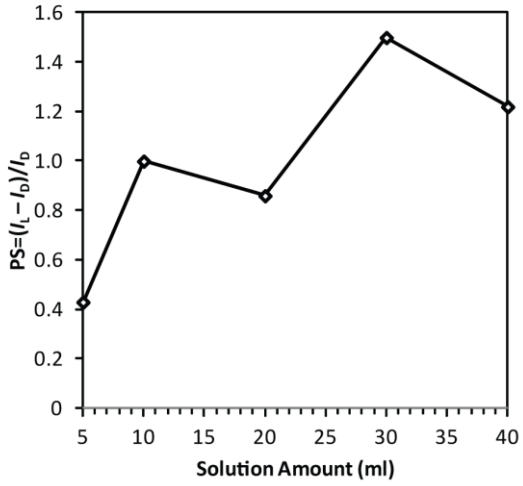

Fig. 7. Variation of photosensitivity values of the films with different amount of solutions

4. Conclusion

$CuInS_2$ thin films have been successfully deposited on soda lime glass substrates using very low amount of spraying solution. All our samples had typical XRD peaks of chalcopyrite $CuInS_2$ crystal. Regardless of the solution amount, polycrystalline $CuInS_2$ thin films were observed. XPS and EDAX results confirmed that elemental composition of the films did not change drastically with solution amount. However, Cu rich secondary phases on the surface were observed for the films deposited using solution amount more than 20 ml. Solution amount by implication thickness of the film is critical for film properties. By using ultrasonic impact nozzle deposition yield of $CuInS_2$ thin films increased drastically while preserving the film quality. It should be noted that using ultrasonic impact nozzles could lower the solution consumption, which is a key for commercialization and large area application of spray deposited solar cells. According to best of our knowledge 0.015 ml/mm^2 solution consumption (30 ml for 26x76 mm^2 area) to achieve 1.95 μm thick films obtained in this study is the highest deposition rate reported in literature. Hence spray pyrolysis deposition of $CuInS_2$ films is very promising to fabricate absorber layer for thin film solar cell applications.

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